Thermodynamics Notes

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Although Newton's laws of mechanics were extremely successful in explaining many natural phenomena, there still remained many processes in nature that could not be understood solely by application of those laws. One of the best known of these other phenomena was heat. Although various attempts had been made to understand heat from at least the time of Aristotle, most of our present knowledge of heat was developed in the nineteenth century. At the core of the development of the thermodynamics in the nineteenth century are the concepts of "energy" and "entropy".

Energy is what makes it go. (1st law)
Entropy tells it where to go. (2nd law)

[The heat supplied is equal to the increase in internal energy of the system plus the work done by the system. Energy is conserved if heat is taken into account.]
[The entropy of an isolated system increases in any irreversible process and is unaltered in any reversible process. This is the principle of increasing entropy.]

According to the **conservation of energy** law, also known as the first law of thermodynamics, energy can be neither created nor destroyed. Thus, the total energy of an isolated system must remain constant. The total **internal energy (E)** of a system—is a **state function** because its value depends only on the present condition of the system, not on how that condition was reached.

Work (w) is defined as the distance moved times the force that produces the motion. In chemistry, most work is expansion (PV work) done as the result of a volume change during a reaction when air molecules are pushed aside. The amount of work done by an expanding gas is given by the equation $w = -P\Delta V$, where P is the pressure against which the system must push and ΔV is the change in volume of the system.

The total internal energy change that takes place during a reaction is the sum of the heat transferred (q) and the work done (-PΔV). The equation of first law

is

$$\Delta E = q + (-P\Delta V) \quad \text{or} \quad q = \Delta E + P\Delta V = \Delta H$$

where ΔH is called the **enthalpy change** of the system, is one of the fundamental equations of thermochemistry. The latent heat of phase change is equal to the difference in ehthalpies of the two phases. [Why the latent heat of vaporization is greater than the latent heat of fusion for the water substance?] In general, the $P\Delta V$ term is much smaller than the ΔE term so that the total internal energy change of a reacting system is approximately equal to ΔH, also called the **heat of reaction**. Reaction that have a negative ΔH are said to be **exothermic** because heat is lost by the system, and reaction that have a positive ΔH are said to be **endothermic** because heat is absorbed by the system. The origin of the word *enthalpy* is the Greek verb *thalpein* meaning "to heat."

In addition to enthalpy, **entropy (S)** —a measure of the amount of molecular randomness in a system—is also important in determining whether a given process will occur spontaneously. Clausius's definition of the **entropy** is $\delta q/T = dS$, with T in *absolute thermodynamic temperature*; and the Boltzmann's definition of entropy is $S = k \ln w$, where k is the Boltzmann's constant $k = 1.38 \times 10^{-23}$ J/K and the w the thermodynamics probability function (do not confuse with the symbol w for work.) With the Clausius's definition of S and the fist law of energy conservation and the second law of entropy increase, we have the optimal working efficiency $e = w/q = T_i - T_o /T_i$, where subscripts "i" denotes input and "o" the output. Together, change in enthalpy and entropy define a quantity called the **Gibbs free-energy change (ΔG)** according to the equation $\Delta G = \Delta H - T\Delta S$. The value of ΔG is a general criterion for whether a reaction will take place spontaneously. If ΔG is negative, the reaction is **spontaneous**; if ΔG id positive, the reaction is **nonspontaneous**.

The quantities we use to describe the macroscopic behavior of a system are called properties, observable characteristics of a system. Other names are thermodynamic variables or thermodynamics coordinates. An extremely important concept is that of a **state variable**, a property whose differential is exact (depends only on the initial and final state but not on the intermediate processes.).

Properties are **extensive** or **intensive**. An **extensive** property is proportional to the mass. An example is the volume V; if the mass is doubled, the volume is

doubled (assuming that the density remains constant). An **intensive** property is independent of the mass. Temperature T is an intensive property; its value is not affected by a change of mass. Pressure P and density ρ are further example of intensive properties. Inherently extensive properties are given by capital letters and intensive properties are denoted by lowercase letters. There are two important exceptions; the temperature T is always capitalized to avoid confusion with the time t, and the pressure P is capitalized to distinguish it from the probability p. An extensive property can be converted to an intensive property by dividing by the mass. The called a specific value:

Specific value = value of the extensive property/mass of the system.